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Ultrafast Structural Dynamics by X-Ray Diffraction and Structural Spectroscopy

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The ability to observe molecular reactions in real time is expected to aid the exploration of new reaction mechanisms, the development of catalysts, the understanding of biomolecular processes and the control of chemical reactions and material properties on a molecular level. To reach this goal, we have developed a gas-phase x-ray diffraction experiment that uses the ultrashort x-ray pulses from the Linac Coherent Light Source (LCLS) to capture atomic motions within molecules in a dilute gas (< 5 Torr). The delay time dependence of the gas x-ray diffraction pattern is measured in a pump-probe scheme with 267 nm excitation laser and 8.3 keV X-ray probe pulses. Optical excitation prepares 1,3-cyclohexadiene on the excited 1B surface, from where it accelerates past a conical intersection down the 2A potential energy surfaces before opening the ring structure on a 140 fs time scale. A “molecular movie” of the observed dynamics is constructed by comparing ab initio quantum molecular dynamics simulations with the experimental diffraction signal to derive weighted trajectories that provide a good representation of the structural dynamics, with the weighted ensemble of trajectories corresponding to the nuclear flux during the chemical reaction. The x-ray structural data thus provide reaction pathways for which ionization energies can be calculated at each step. We use ultrafast time-resolved multiphoton - ionization photoelectron spectroscopy to measure the travel time required for the molecule to reach certain resonance windows to Rydberg states. By so combining the results from the ultrafast x-ray diffraction with observations from ultrafast (structural) spectroscopy, it appears that we can make significant progress towards the ultimate goal: a comprehensive understanding of the spatially resolved photochemical reaction dynamics.